Title: Testing of PVC Films Produced by the Electro-chemical Combination at Bitterfield with Regard to Their Toxicity

(The title VED is in East German equivalent of corporation--translates literally as "people's own business.")

The article is by Bernt done at the Surgical Hospital at Lennon Street, in Karl Marx City, East Germany.

Development of plastic and its multitudinous application raise problems with regard to its possible toxicity and have been proven not harmful. (Lehmann) But as to some of them it cannot be said with certainty that they present absolutely no danger to the human body.

The most used polyvinyl chloride today is employed in the manufacture of various consumer articles. For example, floor coverings, packaging material, raincoats, tubes, blood transfusion apparatus, sponges, etc.

In the production of polyvinyl chloride mostly organic tin compounds are used as stabilizers. Little is known about the toxicity of tin as yet. Researchers have found workers who have breathed tin vapors for years. They have found the metal in their lungs, liver, lymph nodes, and spleen, without any indication of poisonous results. Certain tin salts behave differently. For example, tin chloride causes nerve damage. More recent research has shown that the relative harmlessness of tin rests solely upon the fact that it is difficult to

ingest tin into the body in soluable form. The toxicity shows itself most strongly through the use of alkaline derivatives. Stonerbarnes, Janet and Duff (footnote 7) have established that dialkyl tin combinations and trialkyl tin combinations behave differently. Trialkyl tin combinations are significantly more toxic. The effect is primarily on the nerve system. It can cause paralysis, test animals lose weight and die. Accumulation of tin can be shown above all in the spleen, which in many cases has lead to a change in its outer appearance. According to Zeller (see the reference to Oettel in footnotes 5 and 6) tin combinations of the type of tributyl tin can cause strong skin discoloration. Tin stabilizers with long fatty acid chains prove themselves to be the least toxic.

In the Electrochemical factory at Bitterfield, dibutyl tin dichloride is used to stabilize PVC. The end product contains 1.5% of the stabilizer. In the production a fatty acid ester of dibutyl tin is used. Dibutyl tin chloride is first formed during the polymerization of the PVC.

The fatty acid ester and also the dibutyl tin chloride are soluable in almost all organic solvents. Toxicity of the preparation has been tested by Stoner and his co-workers (see footnote 7) in animal tests. While no lethal doses for rabbits and hamsters has been established, for rats it is 100 milligrams for each kilogram of bodyweight by peroral administration.

In contrast to tributyl tin, the toxicity is 100% lower.

Since obtaining the raw materials for the production of tin stabilizers is difficult in the German Democratic Republic, people have attempted to replace tin with lead combinations for use as stabilizers. The PVC produced with these stabilizers differed from that produced with tin stabilizers. This is evidenced by a darker or merky appearance. It is, however, from a technical point of view, fully identical. In contrast to tin, the toxicity of lead has been known for a long time. It is therefore necessary to speak about the evidences of poisoning somewhat more thoroughly. Although the poisonings result mostly from lead vapor, poisonings can also occur after a lengthly absorption of the material in the stomach and digestive tract. The toxic dose has been stated at different levels. It jumps from between 1 and 10 milligrams per day from month long to year long consumption (in humans). Lead is accumulated in the human body from 95 to 97% in the skeleton system, the rest is in the inner organs--above all in the cerebellum. The use of PVC for the production of consumer articles assumes that PVC, even in cases of large ingestion in the human body, will behave completely indifferently. Since in the articles available to us stabilizers with both tin and lead compounds are contained, it must be shown that these metals, the toxicity of which can be taken as shown, come into the body not at all or only in minute doses and that poisonings can be excluded. For testing there are two possibilities:

(1) proof of whether plastic can be dissolved in body fluids and taken up by the body; and

(2) proof of toxic occurrences in animal tests.

Electrochemical Combination at Bitterfield made available the following plastics to us:

(1) SPVC-stabilizer polymer with 1.5% with stabilizers PP (lead salt of a paraphin carbon acid);

(2) SPVC-stabilized polymer with 1.5% stabilizer PT (powder past 80-20 AH compound); and

(3) SPVC-stabilizer polymer with 1.5% of the stabilizer OZS powder past 80-20 AH (dibutyl tin dichloride).

We attempted to establish to what degree the tested plastics are soluable in the digestive juices of the human body. We used human stomach and duodenal fluids. The types of PVC were placed in the fluids. After a period of 24 hours at 37° celcius the determination of the various extracts in the stomach fluids was done using the Windisch table. In the duodenal fluids the determination was done by distillation of the extract. The results are shown in Table 1. To read Table 1 the words "duodenal" "duodenalsaft" is "doudenal fluid" and "magensaft" is "stomach fluid--gastric juices."

Even if only small amounts are provable, it has however been shown, that the absorption in the organism can occur. This is greater in the duodenal fluids as compared to the stomach fluids. The tin stabilizers are more easily dissolved

than the lead stabilizer. Although the substance which went into solution contained various parts of plastic, it is to be assumed, that the main part was the stabilizer and the softening agent. Due to the minimal amount of the dissolved stabilizer, it is hardly to be assumed, however, even in spite of lengthly ingestion of plastic, that any toxic results will occur.

The tests on animals was done on rabbits. There were two series--in the first, plastic was put in two stages in the muscle of the upper thigh and in the other case the animals were fed three times a week for 16 months with a suspended pulverized plastic. Each testing encompassed four animals for each preparation, of which two were fed and two were implanted. The implantation was done in quantities of 5 grams in powder form in the muscle of the upper thigh. Table 2 shows how many grams per kilograms of bodyweight each animal received.

Powder form was chosen because it is assumed that thereby the largest possible absorption surface would be achieved.

Next table shows the left hand column--the average weight of the animal at the time of implantation, right hand column--the amount implanted in grams for each kilogram of bodyweight. [Now on page 348 of articles.] The plastic behaved completely without irritation. The animals developed normally in comparison with test animals. The bodyweight curve showed a constantly climbing line. The feeding was done as with the other animals

with a mixed feed dependent on the season. There were no indications whatever of poisoning. Upon autopsy, the plastic could no longer be found in the tissue. There apparently was a complete absorption of the material. (This sentence apparently concludes with some comment on scar tissue at the place where the plastic was implanted.)

A microscopic examination on the tissue on all organs showed no effect. In accordance with earlier experience that an accumulation of lead occurs mainly in skeletal system and with regard to the inner organs, mostly in the cerebellum, we attempted to find lead in bones and the brain. It has not been established in which organ tin is likely to accumulate, so we sought evidence of it in the liver, brain, and in the bones. Tables 3 and 4 give an overview of the values that were found. Although they are very low, they indeed show that an absorption of the stabilizers from the plastic can occur. (Table 3 is titled evidence of lead in the implanted animals; first column on the left is in the bones, second column is in the brain, and the third column is an abbreviation which I cannot translate.) (Table 4 shows evidence of tin in the implanted animals. All values are given in milligrams per percent of the material tested. There are five columns: bones, brain, liver, kidneys and again the same title which is given above in Table 3, third column, which I believe is the amount which was absorbed or examined totally.

We have in addition attempted to locate lead and tin in the serum in the animal. The values found here lie far below those values given as toxic concentrations for humans. (.04 milligrams per percent). In order to show a lead intoxication, blood pictures were prepared which showed no deviation from the normal, particularly no [vasophile?] spotting could be shown. In addition, the examinations could exclude the possibility of a porphyrinurie. The animals were fed with pulverized suspended plastic. At first a 5% and later a 10% suspension was used. The 10% suspension was prepared with some sort of duodenal fluid. The test conditions were equivalent to those animals which were implanted. Table 5 shows the amount fed each animal by kilogram of bodyweight.

Also here there were absolutely no appearances of intoxication which could be shown. The animals developed completely normally, the bodyweight curve climbed continuously.

The next paragraph deals generally with the condition of animal no. 3 which apparently died of natural causes.

Tables 6 and 7 show the equivalent of concentrations of tin and lead in the organs. Whereas in the implanted animals no lead was found in the bones, now small amounts of lead are present. Only in the case of animal no. 3 which died during the test the values are somewhat higher. The animal was fed with the same amounts as the others but had constantly had a

lower bodyweight, one must assume that it was for this reason that a higher concentration resulted in his body. Its death cannot, however, be directly connected with the test since no appearance of the lead poisoning could be established. Also in the case of the animals fed, blood tests were done for [vasophile?] spotting and testing of the serum for lead and tin. In the latter case the amount was far below the established toxic concentration. In the blood pictures a porphyrinurie could not be established. The plastic concentrations varied somewhat as shown by Tables 2 through 5.

The tests show that in cases of PVC with lead and tin stabilizers probably there will be some absorption of the stabilizers. The administered quantities, particularly in the case of feeding, are very high. If computed for humans it would mean, that, in order to achieve the same accumulation, the quantity on the average of 2,800 grams would have to be taken up by the body in a year. It is hardly to be assumed, that in the normal use of ordinary articles for human use manufactured of PVC, that an absorption could occur in any amount even approaching our tests.

The second article [which begins "Zum Studium" and appeared in 1966, volume 56 of magazine Kunstoff] deals with thermal decomposition of PVC and different apparatuses to measure HCL emissions or a change in color.

No discussion whatever of toxic matters or of ingestion or breathing by humans is mentioned.

PRIVELEGED

DOCUMENT

Bates number UCC065097-065700 has been skipped

PROPOSED PROTOCOL

SINGLE, MASSIVE, ACUTE VINYL CHLORIDE EXPOSURE

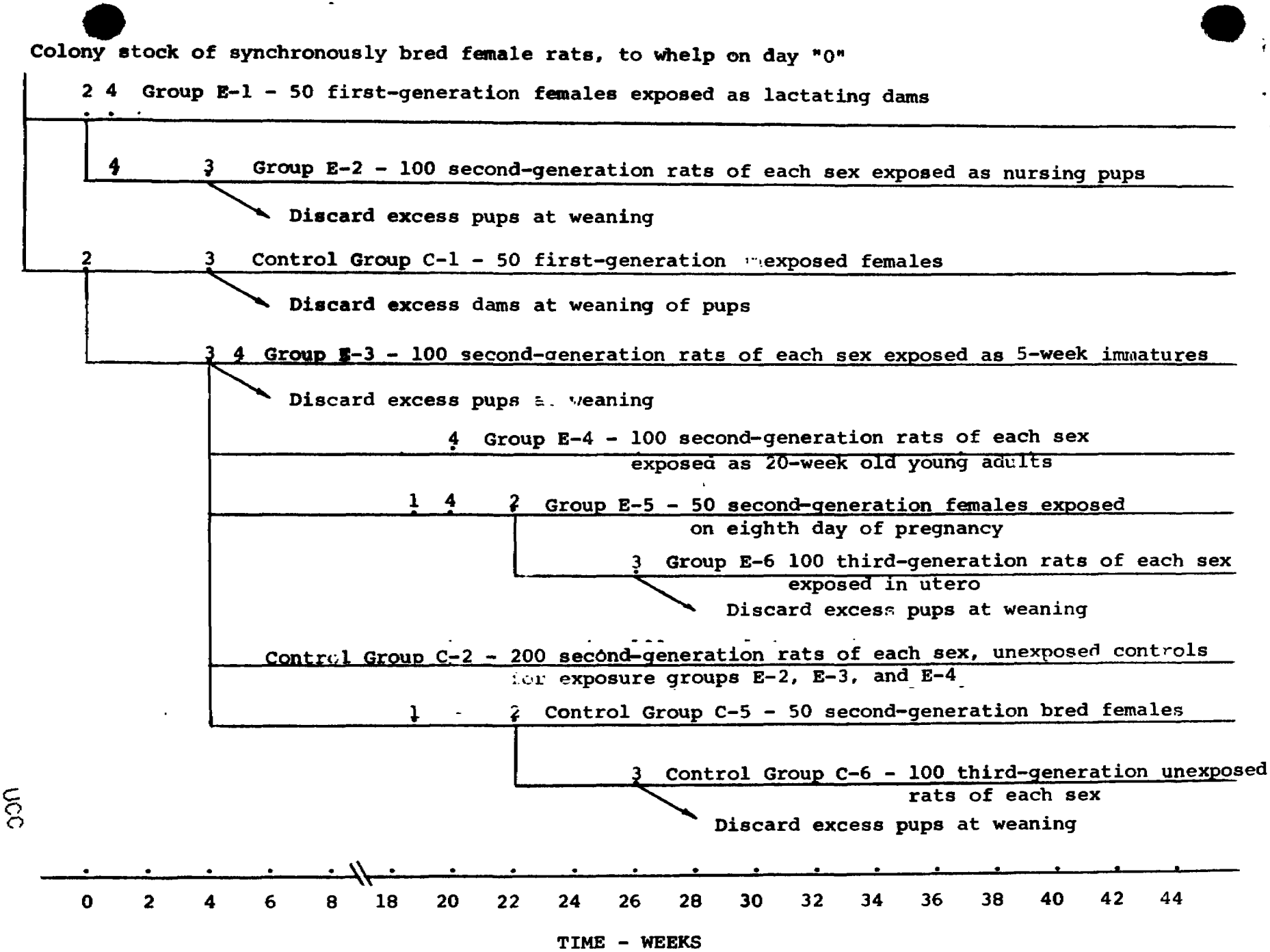
The purpose of this experiment is to evaluate the risk of oncogenesis from the exposure of a community containing a spectrum of age groups to a single, massive dose of vinyl chloride that might result from a "worst credible accident" to tank cars or barge transporting vinyl chloride through an urban area.

It is proposed to expose rats in the following categories to the highest single acute exposure that the most sensitive members of the exposure groups can tolerate without significant acute mortality. The groups will consist of: E-1 -- lactating dams; E-2 -- nursing pups; E-3 -- immature rats of both sexes; E-4 -- young adults of both sexes; E-5 -- pregnant (8-day) females; E-6 -- animals exposed in utero as the fetuses of group E-5.

In order to maintain synchrony among the various groups, and thus to minimize the control groups required, it is proposed to start with a colony of synchronously bred females, and to expose selected families from the colony as groups E-1 and E-2 one week after whelping. Control group C-1 would be ramdomly selected from other members of the colony, and the remainder of the first generation colony sacrificed after weaning of their pups.

All remaining test and control groups would be selected from the second generation animals or their offspring as portrayed schematically on the attached flow sheet.

All animals would be observed for the remainder of their normal life spans, and surviving animals then sacrified for histological study.



UCC 065103

Legend: 1 = time of breeding, 2 = time of whelping, 3 = time of weaning, 4 = time of exposure

PRIVELEGED

DOCUMENT

Bates number 400 093 104-065 105 has been skipped

1. ~~Mr. M. E. Eisenhour~~ Texas City Plant

2. ~~Mrr R. N. Wheeler South Charleston Plant~~

3. Dr. W. R.Manning-Building2000 Tech.Center-South Chas.

You may find of interest. Not warning on peroral dose rate. May wish to file with the Food Produc55 project .

ABSteele

RECEIVED
SEP 27 1971
M. E. EISENHOUR

RECEIVED
SEP 29 1971
R. N. WHEELER

UCC
065106

Confidential
Special Report 34-71

R: 9-1-71

Chemical Hygiene Fellowship
MELLON INSTITUTE
Carnegie-Mellon University

Miscellaneous Toxicity Studies

Editor: C. S. Weil
For: UNION CARBIDE CORPORATION, Chemicals and Plastics Operations Division

SEVIN and/or Phenothiazine

Samples 33-162 and 33-56
Peroral, Single Dose to Female Rats
SEVIN LD50 = 0.224 (0.117 to 0.432) gm/kg; 1 ml = 0.05 gm in corn oil
Phenothiazine LD50 = 2.99 (2.02 to 4.42) gm/kg; 1 ml = 0.25 gm in corn oil
SEVIN plus Phenothiazine LD50 = 0.933 (0.631 to 1.38) gm/kg; 1 ml = 0.30 in corn oil
Predicted/observed = 0.978/0.933 = 1.05; additive joint action.

TEMIK Oxime

2-Methyl-2(methylthio)propionaldehyde oxime
Sample 34-113
Peroral, Single Dose to Rats
LD50 = 0.707 (0.281 to 1.78) ml/kg, undiluted.

UC 30948

2-Methyl-2-[2-methyl-2-(methylthiopropylideneaminoxy]propionaldehyde O-(methylcarbamoyl)oxime
Sample 34-107
Peroral, Single Dose to Rats
LD50 = 0.0238 (0.00952 to 0.0594) gm/kg; 1 ml = 0.05 gm in PEG-400
A D.O.T. Class B poison perorally.

UC 44123

2',6'-Diisopropyl-3',5'-dinitro-2,2,2-trichloroacetanilide
Sample 34-112
Peroral, Single Dose to Rats
LD50 > 5.0 gm/kg; 1 ml = 0.20 gm in PEG-400
Skin Irritation, Rabbit, Uncovered
No irritation on 5 rabbits from 20% in PEG-400
Eye Irritation, Rabbit
No, or trace, irritation from powder or 20% in PEG-400.

UC 46207

2-[O-(methylcarbamoyl)oximino]-1,4-dithiane
Sample 34-128
Peroral, Single Dose to Rats
LD50 = 0.0154 (0.0114 to 0.0208) gm/kg; 1 ml = 0.10 gm in corn oil
A D.O.T. Class B poison perorally.

Vinylidene Chloride
Sample 32-222
Peroral, Single Dose to Rats
LD50 = 0.406 (0.295 to 0.559) ml/kg undiluted.
Inhalation - 4 Hour LC50 = 38,060 (24,940 to 58,070) ppm.
Repeated Peroral Dosing Aimed at Finding any Circulatory Disturbances in Toes or Tail

Groups of 10 male and 10 female, Harlan Wistar, 90 to 120 gram, weanling rats were given undiluted vinylidene chloride by daily stomach intubation to a maximum of 29 doses. The dosage schedule was as follows:

Gm/Kg	Days	Gm/Kg	Days
0.203	7	0.511	3
0.256	3	0.644	2
0.323	5	0.811	3
0.406	2	1.02	2
		1.28	2

Animals received various dosages before death or sacrifice ensued. Cumulative dosage ranged from 3.8 ml/kg to 14.5 ml/kg.

Tissues were taken from the rats that died or that were killed for histopathological examination. The pathologist reported lesions related to gastritis, enteritis and esophagitis with some being sufficiently severe to become perforating ulcers. Particular attention was paid to the toes and tails based on the hypothesis that if this compound was implicated in acro-osteolysis that circulatory failure and lesions of the most distal portions of the body would be affected as is the case in man. No single lesion occurred with sufficient frequency to implicate the compound in this regard. Detailed reports on pathology are available.

Protocol sheets and Standard Test Procedures are available for each entry upon request.

Carol S. Weil

Carrol S. Weil, M.A.
Senior Fellow

Approved:

Charles P. Carpenter

Charles P. Carpenter, Ph.D.
Administrative Fellow

Typed: September 13, 1971 - md

Vinylidene Chloride

M. I. Sample No. 32-222 Initiator A. B. Steele

Data Started 10-20-69 Sample Identification

Peroral, Single Dose to Rats

LD50 - 0.406 (0.295 to 0.559) ml/kg, undilutad.

Conditions - standard.

Dosage; ml/kg	Dead / Dosed	Days to Death	Weight Change	Signs and/or Symptoms
1.0	5/5	0,0,0,0,0	-	Abdomen's distended - death in 3 h urs.
0.5	4/5	2,2,3,3,	+49	At autopsy intestinal irritation. One rat had blood on genitalia and one had a dark red spot on the tail.
0.25	0/5	-	81 to 104	

Conclusions - highly toxic following acute peroral administration.

Inhalation, Single, by Rats

Conditions - Procedure D.

Procedure	Time	Concentration	Dead / Dosed	Days to Death	Weight Change	Signs and/or Sympt ms
D	1.5 hrs	64,000 ppm.	6/6	All in exposure.	-	All prostrate at 8 min.
D	4 hrs	32,000 ppm.	2/6	1 in exposure, 1 at 1 day.	+31 to +53	Poor coordination at 8 min. Prostrate at 45 min.

Gross Pathology - Victims - scattered hemorrhage of lungs, capillary injection in oviducts.
Survivors - large, dark spleen; light brown areas on lungs.
Conclusions - 4-hour LC50 = 38,060 (24,940 to 58,070) ppm.

FOR DESCRIPTION OF TESTS REFER TO STANDARD TEST PROCEDURES

Standard Test Procedures

In all tests, the nonfasted animals are maintained on appropriate Rockland diets and water ad lib except during period of manipulation or confinement. Dosage levels differ by a factor of 2 in a geometric series. LD50s or LC50s are calculated by the moving average method based on a 14-day observation period.

Peroral. Compounds administered by stomach intubation to Wistar derived male rats, 90-120 grams in weight and 3 to 4 weeks of age, reared in our own colony.

Skin Penetration. Male albino rabbits, 3 to 5 months of age, are immobilized during the 24-hour contact period with the compound retained under impervious sheeting on the clipped intact skin of the trunk. Thereafter, excess fluid is removed to prevent ingestion. Maximum dosage that can be retained is 20 ml./kg.

Inhalation. Procedure A. Concentrated vapor is generated in a gas washing bottle by passing dried air at 2.5 liters/min. through a fritted glass disc immersed to a depth of at least 1-1/2 inches in the chemical which is delivered to rats in a 9-liter glass exposure chamber. Mean vapor concentration is calculated from the loss in weight of the liquid or estimated from the vapor pressure at the actual temperature of the chemical during aeration.

Procedure B. Substantially saturated vapor is prepared by spreading 50 grams of chemical over 200 $cm.^2$ area on shallow tray placed near the top of a 120-liter glass chamber which is then sealed for at least 16 hours while an intermittently perated fan agitates the internal chamber atmosphere. Rats are then introduced in a gasketed drawer-type cage designed and operated to minimize vapor loss.

Procedure C. Mist, vapor and any oxidation or decomposition products of the chemical held at 170°C. are generated and delivered as in A.

Procedure D. Vapor at metered concentration, not checked analytically, is generated by feeding the liquid at a constant rate down the inside of a spirally corrugated surface of a minimally heated one inch Pyrex tube, through which metered air is passed. Resultant vapor is delivered as in A.

Procedure E. Spray - Solutions or suspensions are atomized in a glass VAPONEFRIN nebulizer using dried compressed air at 9 liters/min. (corrected) and 22 p.s.i. The resultant aerosol of droplets averaging 2 microns in diameter is conducted directly into a 60-liter cubic glass chamber containing rats. Mean aerosol concentration is calculated from the amount of material atomized.

Procedure F. Dust - Dust clouds are generated by a baffled Wright Dust Feed through which air is passed at 20 liters/min. (uncorrected) at 15 p.s.i. The dust is delivered directly to a 120-liter plexiglas chamber containing rats. Airborne dust concentrations are measured gravimetrically every half hour.

Skin Irritation. Chemical is applied in 0.01 ml. amounts to clipped, uncovered intact skin of 5 rabbit bellies either undiluted or in progressive dilutions of 10, 1, 0.1, and 0.01% in solvent. Ten grades are recognized based on appearance of moderate or marked capillary injection, erythema, edema or necrosis within 24 hours. No injury from undiluted = Grade 1.

Eye Irritation. Eyes not staining with 5% fluorescein in 20 seconds contact are accepted. Single instillation of 0.005, 0.02, 0.10 or 0.5 ml. undiluted or of 0.5 ml. of 40, 15, 5 and 1% dilutions are made into conjunctival sac of 5 rabbits. Read immediately unstained and after fluorescein at 24 hours, with ten grades recognized. Trace or no injury from 0.5 ml. undiluted = Grade 1.

MAILING LIST

Summary f the Miscellaneous Toxicity Studies Report is being mailed to the following List B and Agricultural Chemicals List.

List B

Medical Directors

4 - C. U. Dernehl
1 - E. Q. Hull
1 - R. E. Joyner
1 - T. N. Spencer
1 - R. J. Sexton

Other Distributions

1 - M. B. VerNooy
2 - N. H. Ketcham
1 - P. W. McDaniel
1 - H. R. Guest

Libraries

2 - Chemicals Division (1 set each Library) Building 701 and 770 Libraries, South Charleston, W. Va.

Agricultural Chemicals

1 - R. C. Back
1 - W. J. Bartley
1 - R. A. Bleidt
1 - J. A. Durden
1 - J. B. Harry
1 - R. A. Hensley
1 - D. L. Heywood
1 - H. E. Johnson
1 - F. G. Kennedy
1 - R. L. Meeker
2 - H. H. Moorefield
1 - R. H. Wellman

Library

1 - Union Carbide Corporation
Library - Building 740
P. O. Box 8361
South Charleston, W. Va.

The summary of this report will be included in the COLLECTED SUMMARIES for the month of Sept. and mailed to the following List A.

List A

1 { G. H. Daniels, R. I. Hoaglin, J. J. Smith }
1 - T. T. Szabo
1 - T. H. Welch
1 - N. L. Zutty
1 - J. V. Murray, Jr.
1 - Leon Shechter
1 - Plastics Division Library
Bound Brook, N. J.
1 - Mining and Metals Library
Tuxedo, N. Y.
2 - Chemicals Division Library
Bldg. 701 & 770 Libraries
South Charleston, W. Va.
1 - R & D Library
Tarrytown, N. Y.
1 - W. B. Ackart
1 - E. A. Barr
1 - F. W. Tauber

Pertinent protocol sheets and Standard Test Procedures, along with the Summary pages, are being mailed to the following project initiators:

Project Initiators

1 - J. K. Chan
1 - J. F. Lacount
1 - A. B. Steele

ACTS/VCM/WG/GN/83/5

NOT FOR PUBLICATION

24 AUGUST 1984

GUIDANCE NOTE EH

VINYL CHLORIDE: TOXIC HAZARDS AND PRECAUTIONS

(a) are employed in works in which vinyl chloride is produced, reclaimed, stored, discharged into containers, transported or used in any way whatsoever or in which vinyl chloride is converted into vinyl chloride polymers, and

(b) are likely to be affected by exposure to vinyl chloride in a working area.

5 VINYL CHLORIDE IS HIGHLY FLAMMABLE AND PRESENTS A CONSIDERABLE FIRE AND EXPLOSION HAZARD; THIS GUIDANCE NOTE DOES NOT GIVE ADVICE ON SUCH RISKS. Vinyl chloride comes within the group of substances defined in Class 2 of Part II of Schedule 1 of the Notification of Installations Handling Hazardous Substances Regulations 1982. It also comes within the definition of a flammable gas as set out in Schedule 1(c)(i) of the Control of Industrial Major Accident Hazards Regulations 1984. Some of the requirements of thes Regulations overlap with certain sections of this Guidance Note. Where this occurs reference is made in the text and the Regulations should be consulted for further details.

6 This Guidance Note does not give detailed advice on the control of emissions of vinyl chloride to the atmosphere. HM Industrial Air Pollution Inspectorate is responsible for the control of air pollution arising from industrial processes involving the production of PVC and copolymers from vinyl chloride monomer. For detailed guidance on the control of emissions, reference should be made to the HSE Note on Best Practicable Means BPM 3/79 : Petroleum Works (PVC Polymer Plants).

PROPERTIES OF VINYL CHLORIDE

7 The properties of vinyl chloride are set out in Appendix 1.

HEALTH HAZARDS

8 Vinyl chloride is a gas at room temperature and atmospheric pressure and the most common route of absorption into the body is by inhalation.

Throughout the world there will have been variations around these figures because of differences in plant design or process operation.

RESPONSIBILITIES

13 Employers must do all that is reasonably practicable to safeguard the health of their employees and others who may be affected by work activities involving vinyl chloride. In particular, they have a duty to comply with the provisions of the Health and Safety at Work etc. Act 1974, the Control of Substances Hazardous to Health Regulations 198- and the ACoP on Vinyl Chloride. Employers may also have a responsibility to comply with the Factories Act 1961 and other associated health and safety legislation (see Appendix 5).

14 Section 2(3) of the HSW Act requires employers, with certain exceptions, to prepare, and revise as appropriate, a written statement of their general policy with respect to the health and safety at work of their employees and the organisation and arrangements used to carry out that policy and to bring the statement and any revision of it to the notice of all of their employees. The arrangements within the organisation for a formal system of joint consultation between management and employees and their representatives on all aspects of the Approved Code of Practice on Vinyl Chloride should also be set out in the safety policy.

15 In the safety policy, a member of senior management should be given responsibility for ensuring that the matters covered by the Vinyl Chloride ACoP, the Health and Safety at Work etc. Act and the Factories Act, etc are implemented. These include the responsibility for safe systems of work, safe places of work, training, monitoring, emergency procedures, joint consultation etc. He should be provided with appropriate support as may be necessary.

16 Responsibility for implementing particular aspects of the Approved Code of Practice and this Guidance Note should be allocated at each appropriate level within the organisation with a clear line of communication from plant operatives to the person in overall charge. Steps should be taken to ensure that individuals understand and accept their responsibilities.

ALARM LEVELS

21 In vinyl chloride monomer manufacturing and polymerisation plants there should be a system for the automatic detection of high levels of airborne vinyl chloride in places where these may occur (see para 54). The following concentrations of vinyl chloride in the atmosphere of a working area should be treated as alarm levels, signalling the need for evacuation and remedial action:-

(a) 15 ppm when measured over a period of 1 hour, or

(b) 20 ppm when measured over a period of 20 minutes, or

(c) 30 ppm when measured over a period of 2 minutes.

Where a continuous multi-point analyser (see paragraphs 40-41) is used, two successive readings above the appropriate concentration will determine the existence of an alarm level, ie 15 ppm over a period of 1 hour and 20 ppm over a period of between 20 and 30 minutes.

ASSESSMENT

22 Under the Control of Substances Hazardous to Health Regulations an employer must not carry on any work which may expose his employees to any substance hazardous to health unless he has made an adequate assessment of the risks to health created by the substance. The assessment involves identifying the nature of the substance, the risks to the health of persons who may be exposed, the nature and degree of exposure which may occur during the cours of work and the steps to be taken to avoid risks to health. In order to ensure effective control of exposure to vinyl chloride, it is necessary to collect and assess adequate data on the circumstances under which exposure may arise. In existing plants, most of these data will already have been obtained. All work activities which may involve exposure should be assessed to identify actual and potential sources of emission of vinyl chloride vapour into the working atmosphere. The nature and degree of exposure should be studied in each case. In Appendix 2, a flow chart sets out a sampling strategy for the assessment of exposure to toxic substances. Assessment permits the formulation of plans for the development and introduction of effective engineering, operational and other measures for the prevention or control of exposure, for the maintenance

previous measurements is already available in relation to a specific work activity or where it may be possible to group employees on the basis of similarity of degree of exposure and type of work done to enable an adequate assessment of likely exposure to be made. It is important to study the pattern of exposure of workers in different jobs and locations over whole workshifts and to identify when and where the highest exposures are likely to occur taking into account the possibility of unusual circumstances such as plant breakdowns or emergencies.

27 It is important to carry out sufficient sampling to enable accurate 8 hour time-weighted average concentrations to be calculated. However, shorter term sampling may assist in the assessment of the performance of engineering controls. The survey of exposures should be extended over sufficient workshifts to ensure that the variability of exposure is adequately studied. Further detailed information and advice is available in HSE Guidance Note EH 42 - 'Monitoring Strategies for Toxic Substances'.

28 It is recommended that the results of the assessment be recorded and a copy provided on request at any reasonable time during working hours to employees and/or their representatives at the place of work.

29 The assessment should be revised whenever there is evidence or reason to suspect that it is no longer valid, as a result of, for example:-

(a) a significant change in the work activity; this could be a change in plant, processes or methods of work that might affect the nature or degree of exposure, such as the raising of process temperatures or changes in engineering controls;

(b) results of air monitoring at the work place revealing an increase in exposure;

(c) data arising from health surveillance;

(d) new information on health risks becoming available.

CONTROL MEASURES FOR MATERIALS, PLANT AND PROCESSES

30 When considering appropriate control measures for reducing exposure to a toxic substance, the first strategy to examine is substitution with less

Cleaning and waste disposal

36 Waste polyvinyl chloride slurry containing significant levels of residual vinyl chloride should be stripped of vinyl chloride prior to suitable treatment of the liquid waste for general disposal. Solid polyvinyl chloride waste should preferably be dried before disposal. Wastes arising from vinyl chloride processes should be handled and disposed of in accordance with the Department of Environment Waste Management Paper No 15: 'Halogenated Organic Wastes - A Technical Memorandum on Arisings, Treatment and Disposal including a Code of Practice'.

AIR MONITORING

37 The objectives of monitoring concentrations of airborne vinyl chloride in working areas are:-

(1) to verify that any technical measures and working procedures maintain adequate control of exposure;

(2) to detect abnormal increases in vinyl chloride-in-air levels which may occur as a result of failure or malfunction of some part of the plant or apparatus, with references to the short term alarm levels for vinyl chloride;

(3) to provide adequate records of the exposure of individuals for the purpose of epidemiology.

38 The arrangements for monitoring require careful planning to achieve effective and efficient use of resources. A formal air monitoring plan should be drawn up and made known to all employees working in areas where vinyl chloride is liable to be present. The plan should contain details of the air monitoring procedures and equipment that are to be used to meet the objectives set out in para 37, including details of:-

(a) the parts of plant, working areas and occupational groups of employees to be monitored;

(b) the type of air sampling to be carried out, eg personal air sampling, fixed point air sampling;

Measuring equipment

44 The sensitivity, range, selectivity and speed of response of an analytical device should be appropriate to the duty it is required to perform. Electrical equipment in flammable atmospheres should be suitably constructed, protected and installed; guidance is available in BS Code of Practice 1003.

45 The following techniques are among those suitable for detection and measurement of vinyl chloride:-

(a) gas chromatography

(b) infra-red absorption analysis

(c) flame ionisation detection

Flame ionisation detection is not specific for vinyl chloride and may therefore give readings which are greater than the actual concentration.

46 Gas samples may be taken by any technique which is recognised and acceptable for the analytical technique to be used.

47 A comprehensive description of the various analytical techniques available for the measurement of vinyl chloride are given in 'The Determination of Vinyl Chloride: A Plant Manual - Analytical Methods for the Control of Vinyl Chloride Concentrations In and Around Manufacturing and Process Plants' published by the Chemical Industries Association Limited, Alembic House, 93 Albert Embankment, London SE1 7TU. Details of one of the personal sampling methods used by HSE are available in MDHS 24 - 'Vinyl Chloride in Air: Laboratory method using charcoal absorbent tubes, solvent desorption and gas chromatography'.

Location of sampling points for fixed analysers or automatic sequential fixed point sampling systems

48 Sampling points should be located within the working area to sample air representative of that breached by the workers. The probes should normally

Alarm systems

54 Whatever sampling system is used for routine monitoring, there should also be a system for the automatic detection of high levels of airborne vinyl chloride in places where these may occur, eg in the event of plant failure. The alarm system may be integrated with a continuously operating or permanent sequential system provided for the purpose of air monitoring.

Recording and presentation of results

55 The results of all atmospheric monitoring at fixed points should be available for inspection by personnel working in areas where vinyl chloride is liable to be present and their representatives at any time during a working period. Where continuously operating multi-point sequential sampling methods are employed, the results should be displayed as far as possible within two hours of the end of each shift sampled. Where discontinuous method and/or personal monitoring are used, the results should be displayed within 24 hours of completion of the sampling period where possible.

56 In the areas where continuously operating multi-point sequential sampling and analysing equipment is installed, results should be summarised on a shift basis for each identifiable work area showing the average concentration in the area. Basic details of the position and number of sampling points together with the frequency of sampling and analytical methods used should be included at the beginning of the series of records and thereafter need only be recorded when changes occur in the monitoring procedure.

57 In the areas where sampling is carried out other than on each shift, the individual time weighted average results should be recorded. These should be summarised on a monthly basis showing the average concentration at each location with an analysis of the distribution of the individual results.

58 Records of maintenance and monitoring should provide sufficient information to enable employers, self employed persons, persons in control of premises, employees and/or their representatives at the workplace, and enforcing authorities to:-

(c) instruments used and results of instrument readings;

(d) defects noted;

(e) action taken;

(f) name, signature and appointment of person making examination.

(3) Excursions above the alarm levels as detected during area monitoring

(a) part of factory to which the record refers;

(b) precise location within the factory;

(c) date, time and (where known) duration;

(d) maximum time weighted average concentrations recorded;

(f) result of investigation;

(g) action taken;

(h) name signature and appointment of person making inspection.

(4) Personal monitoring

(a) name of employee;

(b) date;

(c) time and duration of exposure;

(d) time weighted average concentrations recorded;

(e) precise duty and working area within factory;

(f) nature and nominal efficiency of respiratory protective equipment (if worn).

64 In particular, adequate and suitable breathing apparatus must be worn:-

(1) when it is not reasonably practicable to remove vinyl chloride vapour by local exhaust ventilation, e.g. when opening equipment which may release appreciable quantities of vinyl chloride to the atmosphere and during the maintenance or repair of equipment. No such operation should be conducted without a permit-to-work issued by a competent person designated by the employer for this purpose. Precautions should be taken to ensure that other unprotected personnel in the vicinity are not liable to be exposed to concentrations of vinyl chloride above the 8 hour TWA Control Limit;

(2) during entry into confined spaces which have not been certified by a competent person as being safe for entry without breathing apparatus.

65 Following an alarm, adequate and suitable breathing apparatus should be worn by any person remaining in an affected area until the alarm is over. The source of an escape of vapour should be identified and appropriate corrective action taken without delay.

66 It is recommended that no person should be required to rely for protection on respiratory protective equipment unless he has successfully completed a training or refresher course on the use of such equipment within the previous 12 months and has been issued with a certificate to this effect. The training or refresher course could include the following:-

(a) principles of operation and use of equipment;

(b) practical use, correct fitting, etc;

(c) limitations of the equipment;

(d) common defects and action required;

enclosed plant, there may be no need for the wearing of special protective clothing by process workers. However, certain circumstances, such as entry into confined spaces or some maintenance work, may require the use of special protective clothing. Such situations should be identified as part of the general assessment. The standard of clothing necessary will depend upon the nature of exposure. For example, where substantial body contact can be foreseen a high standard of protective clothing should be provided, eg completely enclosing air-fed suits (where respiratory protective equipment is also necessary) of wire reinforced PVC, or overalls of PVC-proofed material, completed in all cases by PVC gloves and boots. Where an area is relatively free of vinyl chloride, having perhaps been cleaned by means of high pressure hoses or other methods, overalls of materials such as terylene or cotton, may be adequate.

PERMITS TO WORK

71 A permit-to-work is essentially a document which sets out the work to be done and the precautions to be taken. It predetermines a safe procedure and is a clear record that all foreseeable hazards have been considered in advance and that all appropriate precautions are defined and taken in correct sequence. It does not, in itself, make the job safe but is dependent for its effectiveness on the persons concerned conscientiously carrying out the requirements of the permit. There should be provision on the permit-to-work for the persons authorising the work to sign to this effect and for the persons carrying out the work to sign the document at each stage of the operation as it is completed. Permits to work should be issued for all entries into confined spaces and for certain maintenance operations. Copies of all permits-to-work issued should be kept for a minimum period of 2 years.

Confined spaces

72 In this Guidance Note the term 'confined space' includes any chamber, tank, vat, pit, pipe, flue or similar confined space such as, for example, a reactor, duct, or bunker in which vinyl chloride vapour is known to be or is liable to be present.

73 Unless adequate precautions are taken, entry into a confined space involves a particular risk of exposure to very high levels of vinyl chloride or lack of oxygen. Concentrations of vapour may even be such as to involve a

If there is a possibility that the proportion of oxygen in the air of a confined space has been substantially reduced no person should enter or remain in such a space unless he is either wearing suitable breathing apparatus. Alternatively the space should be adequately ventilated and a competent person should test and certify it as safe for entry without breathing apparatus.

Maintenance operations

78 When a non-routine operation or malfunction may result in the release of vinyl chloride to the atmosphere, adequate and suitable breathing apparatus of a type approved by HSE should be worn. Wherever possible special measures should be taken to prevent emissions of vinyl chloride. Such operations should not be conducted without permission in the form of a permit-to-work from a competent person designated by the employer for this purpose. Precautions should be taken to ensure that other personnel are not exposed to levels of vinyl chloride above the Control Limit.

MAINTENANCE OF CONTROL MEASURES

79 All plant, especially that from which vinyl chloride may escape or which is provided for the purpose of controlling exposure to vinyl chloride, should be maintained to a high standard in order to limit the exposure of workers to vinyl chloride. Maintenance procedures should include regular and thorough examinations by a competent person at appropriate intervals of those parts of the plant at which leakages of vinyl chloride may develop over a period of time. A suitable instrument giving a direct read-out of the concentration of vinyl chloride-in-air should be used for leak detection during such examinations. All defects found should be remedied promptly and the results of maintenance examinations and details of remedial action taken recorded.

80 Regular examinations and tests should be made of ventilation equipment and other technical control measures by a competent person, using instruments where appropriate, to check the performance of such equipment as part of a planned preventive maintenance programme. Where ventilation plant is provided in pursuance of Regulation 7 of the Control of Substances Hazardous to Health

having consulted the District Inspector. Under the Notification of Accidents and Dangerous Occurrences Regulations 1980 the sudden, uncontrolled release of 1 tonne or more of vinyl chloride, eg. by rupture of a bursting disc, must be notified to the HSE immediately.

REGISTERED WORKERS

83 In plants subject to the requirements of the Vinyl Chloride ACoP, any worker identified during the assessment procedure required under Regulation 6 of the Control of Substances Hazardous to Health Regulations as likely to be affected by occupational exposure to vinyl chloride should be designated as a 'registered worker'. A register of such workers should be kept by the employer. Any worker generally spending less than 25% of his working year exposed to vinyl chloride need not be designated as a registered worker. Consideration should also be given to designating other persons working regularly on site, eg contractors' employees, as registered workers where there is the potential for exposure to vinyl chloride on a scale similar to that for an employer's own employees and the assessment warrants such action.

HEALTH SURVEILLANCE

84 Health surveillance of registered workers is intended to detect, as early as possible, any harmful effects associated with exposure to vinyl chloride at work. The initial assessment considers the individual's fitness to work with vinyl chloride and establishes baseline medical information with regard to registered workers.

85 Workers should be subject to periodic assessment to check their fitness to continue working with vinyl chloride. The assessment may also provide additional information which might lead to a fuller understanding of the toxicological effects of vinyl chloride. Such data could also be of value in any future epidemiological studies. Each person should be subject to medical reassessment:-

(a) at intervals of not more than 12 months;

Where the number of employees to be examined or assessed is substantial, a suitable waiting area should be provided. An adjacent lavatory with hand-washing facilities should be provided for employees who may be required to provide specimens for biological testing.

90 Arrangements should be made for any employee who is a registered worker to present himself, during his normal working hours, for medical examinations and any additional tests as may be necessary. Employees should cooperate in such examinations and tests.

91 The basic occupational health record of a registered worker's health surveillance should consist of at least the following information:-

surname, forenames, birth surname, sex, date of birth, place of birth, (town and country), permanent address, National Insurance Number, National Health Service Number, data of commencement of present employment, and a historical record of jobs performed whilst in that employment, with appropriate details to indicate likely exposure.

92 These records may be kept in any suitable form provided that they satisfy the foregoing requirements and can be retrieved readily when required. They should be kept in a form compatible with and capable of being linked to those for monitoring, so that it is possible to compare the nature and degree of exposure to vinyl chloride with effects on health. The health record of a registered worker should be kept for at least 50 years from the date of the last entry.

93 Some of the conditions associated with exposure to high levels of vinyl chloride, particularly angiosarcoma of the liver and portal hypertension due to non-cirrhotic periportal fibrosis, may have prolonged latent periods with symptoms not appearing until several years after exposure, possibly after a vinyl chloride worker has retired or transferred to other work. In all cases when a vinyl chloride worker leaves a company, ceases to be a registered worker or transfers to another location, a letter should be sent to his Family Practitioner by the Appointed Doctor. Appendix 3 contains a suggested letter for sending to an employee's Family Practitioner and Appendix 4 a suggested form for the employee to give his consent for the Appointed Doctor to discuss his medical and occupational history with regard to his exposure to vinyl

(e) role of the employee in observing safe working methods;

(f) correct use of respiratory protective equipment and any other personal protective equipment;

(g) significance of monitoring procedures and results;

(h) relevant emergency procedures;

(i) relevant rules relating to vinyl chloride;

(j) procedures for reporting defects in plant and equipment.

It should be noted that Regulation 4 of the Control of Industrial Major Accident hazards Regulations 1984 requires a manufacturer to provide evidence that persons working on a site are informed, trained and equipped as necessary to ensure their safety.

96 Basic information, instruction and training should be provided on recruitment and should be supplemented at regular intervals by training, "on-the-job" refresher courses, talks, notices, leaflets or other methods in order to create and sustain a high level of awareness amongst employees.

97 Any person who carries out any assessment, air monitoring or maintenance tasks which require the use of instruments should be given additional instruction and training concerning their use including:-

(a) objectives of air monitoring;

(b) correct use of the instruments;

(c) sampling techniques;

(d) analysis, interpretation and recording of results.

notification to HSE of any site handling quantities of vinyl chloride in excess of 25 tonnes with renotification at three times this figure. Vinyl chloride also comes within the definition of a flammable gas as set out in Schedule 1 e(i) of the Control of Industrial Major Accident Hazards Regulations 1984. Notification to HSE is required under Regulation 4 at 50 tonnes of vinyl chloride and for Regulations 7-12 at 200 tonnes for process and storage or 300 tonnes for isolated storage. Notification to HSE is also required of significant modifications to the industrial activity for inventories exceeding 200 or 300 tonnes for process and storage or isolated storage respectively. For further details, reference should be made to the appropriate Regulations (see Appendix 6) and associated guidance published by HSE.

RECORDS

103 There are a number of references in various sections of this Guidance Note to the keeping of registers and records. For ase of reference these requirements are summarised in Appendix 5.

104 Where an employer ceases to operate, it is recommended that the Health and Safety Executive be notified and the records of air monitoring and employees' occupational health records transferred to HSE.

APPENDIX 3

Dear Doctor

CONTROL OF SUBSTANCES HAZARDOUS TO HEALTH REGULATIONS 198-
APPROVED CODE OF PRACTICE FOR THE CONTROL OF VINYL CHLORIDE AT WORK

Mr/Mrs/Miss .....

Date of Birth .....

Address .....
.....

is about to leave/has just left employment here where he/she was registered as a worker potentially or actually exposed to vinyl chloride monomer (VCM).

Exposure to high levels of VCM has been associated with angiosarcoma of the liver, portal hypertension due to non-cirrhotic periportal fibrosis and acro-osteolysis particularly of the terminal phalanges of the hands.

Other effects have been reported as occurring in workers chronically exposed to vinyl chloride monomer at similar levels of exposure, although such reports have been disputed by others. These include tumours of the brain, lung, haemo-lymphopoietic system, and skin (malignant melanoma), lung function disorders, thrombocytopoenia and immune complex disorders. Effects on reproduction have also been reported.

Whilst exposure to such levels is unlikely to have been incurred since 1975, the latent period particularly for the first two above mentioned conditions may be prolonged.

May I therefore suggest that this letter which (together with the patients form of consent) has been approved by the General Medical

APPENDIX 4

CONTROL OF SUBSTANCES HAZARDOUS TO HEALTH REGULATIONS 198-
APPROVED CODE OF PRACTICE FOR THE CONTROL OF VINYL CHLORIDE AT WORK

MEDICAL SURVEILLANCE

(Give surname and full fore-names, give date of birth thus eg 3 SEPT 36

I, ... born .....

of .....

.....

hereby give consent for the Appointed Doctor or the Area Employment Medical Adviser to discuss with my family doctor my medical and occupational history and I also consent to the release to my family doctor of such records insofar as they relate to my exposure to Vinyl Chloride Monomer.

I confirm that Dr ....., Appointed Doctor has explained to me the reasons for this consent being sought and I believe that I have understood these reasons. I agree to a copy of this consent and explanatory letter, which I have seen, being sent to my present family doctor, Dr ....., of .....

Signed .....

Date .....

Witness .....

APPENDIX 6

LEGAL REQUIREMENTS

Some additional legal requirements relevant to the handling of vinyl chloride may be found in the following:-

The Health and Safety at Work etc Act 1974
The Factories Act 1961
The Alkali etc Works Regulation Act 1906
The Emissions into the Atmosphere Regulations 1983
The Control of Pollution Act 1974
The Control of Substances Hazardous to Health Regulations 198_
The Notification of Installations Handling Hazardous Substances Regulations 1982
The Control of Industrial Major Accident Hazards Regulations 1984
The Dangerous Substances (Conveyance by Road in Road Tankers and Tank Containers) Regulations 1981
The Dangerous Substances (Conveyance by Road in Packages etc.) Regulations 198-
The Classification, Packaging and Labelling of Dangerous Substances Regulations 1984
The Notification of Accidents and Dangerous Occurrences Regulations 1980
The Reporting of Accidents and Dangerous Incidents Regulations 198-

EMERGENCY PLANNING (Paras 81-82)	- Suitable plans required to deal with foreseeable emergencies - All employees should be familiar with relevant emergency procedures
HEALTH SURVEILLANCE (Paras 84-94)	- Registered workers should undergo regular medical examinations
INFORMATION, INSTRUCTION & TRAINING (Paras 95-97)	- All employees should receive adequate information, instruction and training on the hazards of vinyl chloride, the precautions to be observed and the role of joint consultation